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GEOCHEMISTRY

Evolution of Mineral-Forming Fluids at the 9–10° N and 21° N East Pacific Rise Hydrothermal Systems: Fluid Inclusion Data on Minerals

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Significant variations in temperature and chemical and isotopic composition were found by direct measurements in the mineral-forming fluids that make up sulfide mounds in the active hydrothermal fields confined to spreading centers [1, 2]. Sulfide–sulfate ores from a single source are precipitated over several tens of years, while physicochemical parameters vary more frequently than are measured. The study of fluid inclusions in the minerals from some sulfate–sulfide mounds revealed the wider variations in the mineral formation temperature and salinity of the mineral-forming fluids, as compared to those obtained by direct measurements in fluid seepages [3]. The degree, modes, and causes of variations in chemical composition and fluid temperature are urgent issues. In order to solve them, we investigated samples taken from the 9°–10° N and 21° N East Pacific Rise (EPR) areas using the *Mir* manned submersible during Cruise 49 of the R/V *Akademik Mstislav Keldysh* in 2003. We carried out for the first time microthermometric study of the fluid inclusions in anhydrite, gas-chromatographic analysis of hydrocarbons, determination of He isotopic composition of fluid inclusions in sulfides, and determination of the sulfur isotope composition in sulfides from sulfide mounds.

The sulfide mounds at 21° N EPR were found in autumn of 1978 [4]. Active hydrothermal vents were found in this area in 1979 [5]. Subsequent studies over more than 23 years showed that fluid seepages from the sulfide mounds in this hydrothermal field have stable chemical composition. At 9°–10° N EPR, the study of hydrothermal activity was begun immediately after a volcanic eruption in 1991. The monitoring of active vents showed that the salinity and temperature of the fluid significantly changed over the past 13 years [2]. Repeated lava eruption on May 2006 partially buried some mounds. Thus, the study of samples from these mounds provides unique insight into the evolution of mineral-forming fluid for a geologically instantaneous time span.

The fluid inclusions were studied in samples 4683-2 (part of the sulfate–sulfide plate with lenses of crystalline anhydrite) and 4683-6 (top of the active sulfide pipe) at the 21° N EPR hydrothermal field and 4669-2 (fragment of the active sulfide–sulfate mound P) at the 9° N EPR hydrothermal field. The fluid inclusions 5–60 μm in size are allocated by growth zones of the anhydrite crystal along the faces or evenly over the mineral, signifying their primary origin. Their shapes are different: flat elongated, rectangular tabular, or rounded flattened pipelike. At room temperature, all fluid inclusions are two-phase formations consisting of transparent light liquid and gas bubble.

The microthermometric studies of fluid inclusions were performed using heating and freezing stages of an original design [6]. More than 120 homogenization temperatures and more than 70–110 ice melting temperatures were measured in each sample. Fluid inclusions in the sample from 9° N EPR were frozen at temperatures from –45 to –52°C. The eutectic temperature varied from –29.5 to –38.5°C, which indicates that dissolved salts are dominated by NaCl with subordinate $MgCl_2$. Fluid salinity estimated from ice melting varies from 4.0 to 12.6 wt % NaCl equiv (Fig. 1a). The eutec-

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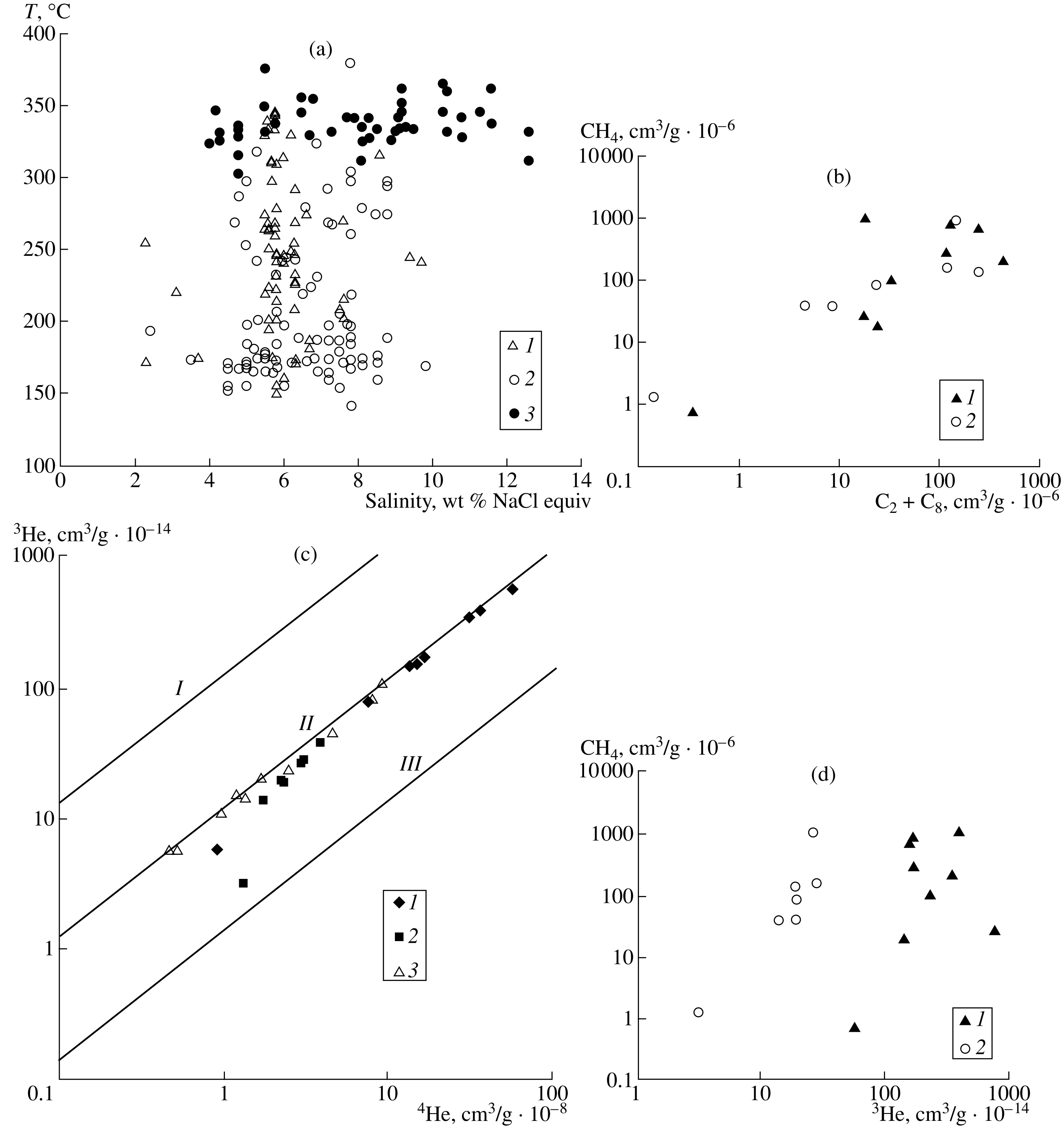

Plots for fluid mineral-hosted inclusions in sulfate–sulfide ores from the 9°–10° N and 21° N EPR hydrothermal fields: (a) homogenization temperature vs. salinity in the anhydrite-hosted fluid inclusions, (b) methane content vs. total content of heavy hydrocarbons, (c) ^{3}He vs. ^{4}He, and (d) methane content vs. ^{3}He. (a): (*1*) 21° N EPR, (sample 4683-2), (*2*) 21° N EPR (sample 4683-6), (*3*) 9° N EPR (sample 4669-2); (b, d): (*1*) 9° N EPR, (*2*) 21° N EPR; (c) (*1*) 9° N EPR, (*2*) 21° N EPR (our data), (*3*) 21° N EPR [12]. (*I*) ^{3}He/^{4}He = $1 \cdot 10^{-4}$, R/Ra = 71.4; (*II*) ^{3}H/^{4}He = $1.12 \cdot 10^{-5}$, R/Ra = 8, (*III*) ^{3}H/^{4}He = $1.4 \cdot 10^{-6}$, R/Ra = 1.

tic temperature (from –22.8 to –29.3°C) in the inclusions from 21° N EPR indicates that the solutions were dominated by NaCl. The salinity of fluid entrained in anhydrite from sample 4683-2 is nearly constant (6–6.5 wt % NaCl equiv), though the salinity occasionally sharply changes and decreases to 2.3 wt % or increases to 9.7 wt % NaCl equiv (Fig. 1a). The salinity of fluid in the anhydrite-hosted inclusions from sample 4683-6 showed more significant variations: from 5.0 to 7.8, occasionally from 2.4 to 9.8 wt % NaCl equiv (Fig. 1a).

Hence, the mineral-forming fluid in both hydrothermal systems shows extremely wide variations in salinity, although the variations are sporadic in the 21° N EPR hydrothermal system. It should be noted that these changes proceed differently in different vents of this system.

Upon heating, all fluid inclusions in anhydrite are homogenized into liquid. Inclusions in anhydrite from mound P at 9° N EPR are typically homogenized at 320–376°C, more rarely at 270–310°C (Fig. 1a). Fluid inclusions in anhydrite from the mounds at 21° N EPR are homogenized within a wider temperature range: 150–350°C in sample 4683-2 and 142–380°C in sample 4683-6 (Fig. 1a). The anhydrite from sample 4683-2 is dominated by moderate-temperature (232–305°C) and high-temperature (305–350°C) fluid inclusions, whereas anhydrite from sample 4683-6 contains low-temperature (140–235°C) fluid inclusions. Since inclusions entrained monophase fluids, the homogenization temperature must be corrected for pressure to obtain the true temperatures of mineral formation. The ocean depth in the sampling localities at the 9° N and 21° N EPR were, respectively, 2500 m and 2600 m. Hence, the temperature of anhydrite precipitation is estimated at 285–390°C in the mound of 9°N EPR, and 145–395°C in the mounds of 21° N EPR.

The study of fluid inclusions indicates that variation in the fluid salinity and temperature in the considered hydrothermal systems is significantly wider than was shown by direct measurements periodically conducted using the *Alvin* manned submersible. In the seepage from the vent P at the 9° N EPR hydrothermal field, the temperature and Cl content variation was 357–392°C and 41.6–625 mmol/kg solution, respectively [2]. In the 21° N EPR hydrothermal field (SW zone), the variation was 335–355°C and 472–525 mol/kg solution, respectively [1]. The study of fluid inclusions in sphalerite and anhydrite from the OBS zone [7, 8] showed relatively stable values of fluid salinity (2.9–3.8 wt % NaCl equiv), though the temperature of mineral formation varied significantly from 170 to 350°C.

The performed studies demonstrate an exceptionally wide evolution of salinity and fluid of *black smoker* fluid even during formation of one sulfide mound, i.e., less than 15 years in the 9° N EPR hydrothermal system. These data also contradict the generally accepted viewpoint that the chemistry and temperature of the fluid in the 21° N EPR hydrothermal system has remained relatively stable for more than 20 years.

The study of hydrocarbons dissolved in the mineral-forming fluids was conducted using a Tsvet-102 gas chromatograph. To extract hydrocarbon gases from fluid inclusions, host sulfides were crushed in a miniature vibration chamber inserted in a gas-loading device of the gas chromatograph [9]. Samples of a fraction from –0.63 to + 0.25 mm and 1 g in weight were placed in the vibration chamber. Saturated and unsaturated hydrocarbons were found in the fluids. The saturated hydrocarbons are methane, ethane, propane, and butane, while unsaturated hydrocarbons are represented by ethylene (C_2H_4), propylene (C_3H_6), and butylene (α-C_4H_8 and β-C_4H_8). The hydrocarbon contents vary in different samples. The following contents were found in samples from 9° N EPR ($cm^3/g \cdot 10^{-6}$): 0.76–1035 CH_4, 0.07–148 C_2H_4, 0.18–191 C_3H_6, 35 *i*-C_4H_{10}, 89.2 *n*-C_4H_{10}. Samples from 21° N EPR contain 38.2–980 CH_4, 2.42–79.6 C_2H_4, 1.27–111 C_3H_6, 0.22–19.6 *i*-C_4H_{10}, and 0.32–50.7 *n*-C_4H_{10}. The methane distinctly dominates among hydrocarbons (up to 80–90%) and shows positive correlation with the sum of heavy hydrocarbons (Fig. 1b). In addition to ethane (C_2H_6), the heavy hydrocarbons include relatively high contents of propane (C_3H_8) and normal butane (*n*-C_4H_{10}). The obtained values are not true hydrocarbon concentrations in the mineral-forming fluid. Nevertheless, they indicate that variations took place both within a single vent and in different vents.

The proportions of ^3He and ^4He in the gas phase of fluid inclusions entrained during sulfide crystallization were studied on MI-1201 mass spectrometer [10]. Helium was extracted from 2-g aliquot finely ground in evacuated ampoules, which were unsealed in the gas loading device of the mass spectrometer. The studies showed that the R/Ra ratio, where R is the $^3He/^4He$ ratio in the studied sample and Ra is the $^3He/^4He$ ratio in air equal to $140 \cdot 10^{-8}$, varied mainly from 7.7 to 8.4 (with the exception of one R/Ra ratio equal to 4.61) in fluid entrained by sulfides from mounds of 21° N EPR during crystallization. The R/Ra ratio varied from 5.8 to 7.1 in fluids from mounds at 21° N EPR (Fig. 1c). The ratio was 1.73 in the anhydrite-hosted fluid from mounds at 21° N EPR. The $CH_4/^3He \times 10^6$ values varied from 0.086 to 4.49 in the fluids extracted from sulfide-hosted fluid inclusions at 9° N EPR and from 2.74 to 7.5 at 21° N EPR (up to 37.2 in one sample). These values are quite consistent with data obtained on fluid seepages at the 21° N EPR hydrothermal field (3.5 and 6.5) and basalts (0.7–2.5) [11]. The positive correlation between the contents of CH_4 and ^3He implies a common source of these components (Fig. 1d). It should be noted that the fluid from vents, which make up sulfate–sulfide mounds at 21° N EPR, seemed to be slightly enriched in radiogenic isotope ^4He relative to fluid from the 9° N EPR hydrothermal system and relative to previously obtained data on fluid inclusions from sulfides of 21° N EPR (R/Ra = 7.1–8.0) [12] and fluid taken from the active vent (R/Ra = 7.8) [11]. The R/Ra values of 7.7 and 8.4 obtained for the fluid that produced sulfides of mound P at 9° N EPR are close to the upper mantle $^3He/^4He$ ratio of 8 ± 1. This suggests that He was supplied from the upper mantle owing to its degassing. Anhydrite in mounds of 21° N EPR was precipitated owing to the interaction of Ca^{2+} from high-temperature fluid with seawater SO_4^{2-}. Therefore, the fluid in this mineral is characterized by low R/Ra = 1.4. Anhydrite is replaced by sulfides during mound formation, precipitated in the deep-seated parts of hydrothermal system, and dissolved during repeated percolation of fluid along the fault zone. Therefore, the released radiogenic helium could reduce the R/Ra ratio in the mineral-forming fluid to 5.5 or less. Since the 21° N EPR hydrothermal system has been operating over a significantly longer period than the 9° N EPR counterpart, the content of radiogenic He is higher in the former system. However, mantle He significantly predominates in this system. If He and hydrocarbons were derived from a common source, the hydrocarbons could be formed in the hydrothermal system by the interaction of components produced by mantle degassing.

What processes provoke such significant changes in temperature and salinity of the hydrothermal fluid over such short periods? The monitoring of the 9°–10° N EPR hydrothermal field revealed several events over the last 13 years that could affect the thermal setting and rock permeability. The ^{210}Pb/^{210}Pb dating of basalts [13] and increase of CO_2 content in the fluid [14] attest to new magma eruptions and its degassing in this period. New seismic shocks were also reported in [15]. The hydrothermal fields can be characterized by a fairly rapid change in the magma chamber depth, repeated fracturing, and the emplacement of new dikes. These processes can change the depth of seawater penetration and the reaction zone. Fairly high temperatures of the fluid, which precipitated anhydrite (390°C at 9° N EPR and 395°C at 21° N EPR), point to fluid unmixing at depths of 2500–2600 m. At these temperatures and a pressure of 250–260 bar, fluid with an initial salinity equal to seawater salinity (3.2 wt % NaCl equiv) could intersect the two-phase curve in the H_2O–NaCl system, which caused its exsolution into liquid (relatively saline) fluid (up to 13 wt % NaCl equiv) and low-density low-salinity (gas-rich) phase. The phase unmixing led to sulfur isotope fractionation and He transition into the gas phase. The low-density fluid reached the seafloor more rapidly than the low-density fluid, which can be retained in the deeper parts of the hydrothermal system. Later, it could be mixed with ascending low-salinity fluid, which provoked sharp changes in the chemical composition and temperature of the mineral-forming fluid. Thus, the phase unmixing of the fluid in hydrothermal systems with short-term changes in the depth of the magma chamber, repeated injections of magma, and fracturing serve as very efficient mechanisms for short-term variations in the chemical and isotopic compositions of fluids.

Thus, the study of fluid inclusions in the minerals from fresh sulfides demonstrated that significant variations in the temperatures and chemical composition of the mineral-forming fluid could occur in a geologically instantaneous period. These processes evidently were also typical of the ancient sulfide-forming hydrothermal systems.

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